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14. ABSTRACT Kapton® polyimide (PI) is extensively used in solar arrays, spacecraft thermal blankets, and space inflatable structures. Upon exposure to atomic oxygen (AO) in low Earth orbit (LEO), Kapton® is severely degraded. An effective approach to prevent this erosion is chemically bonding polyhedral oligomeric silsesquioxane (POSS) into the polyimide matrix by copolymerization of POSS-diamine with the polyimide monomers. POSS is a silicon and oxygen cage-like structure surrounded by organic groups and can be polymerizable. The copolymerization of POSS provides Si and O in the polymer matrix on the nano level. During POSS polyimide exposure to atomic oxygen, organic material is degraded and a silica passivation layer is formed. This silica layer protects the underlying polymer from further degradation. Ground-based studies and MISSE-1 and MISSE-5 flight results have shown that POSS polyimides are resistant to atomic-oxygen attack in LEO. In fact, 3.5 wt% Si ₈ O ₁₁ main-chain POSS polyimide eroded about 2 µm during the 3.9 year flight in LEO, whereas 32 µm of 0 wt% POSS polyimide would have eroded within 4 mos. The atomic-oxygen exposure of main-chain POSS polyimides and new side-chain POSS polyimides has shown that copolymerized POSS imparts similar AO resistance to polyimide materials regardless of POSS monomer structure.					
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Space Survivability of Main-Chain and Side-Chain POSS-Kapton Polyimides (Preprint)

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Abstract

Kapton[®] polyimide (PI) is extensively used in solar arrays, spacecraft thermal blankets, and space inflatable structures. Upon exposure to atomic oxygen (AO) in low Earth orbit (LEO), Kapton[®] is severely degraded. An effective approach to prevent this erosion is chemically bonding polyhedral oligomeric silsesquioxane (POSS) into the polyimide matrix by copolymerization of POSS-diamine with the polyimide monomers. POSS is a silicon and oxygen cage-like structure surrounded by organic groups and can be polymerizable. The copolymerization of POSS provides Si and O in the polymer matrix on the nano level. During POSS polyimide exposure to atomic oxygen, organic material is degraded and a silica passivation layer is formed. This silica layer protects the underlying polymer from further degradation. Ground-based studies and MISSE-1 and MISSE-5 flight results have shown that POSS polyimides are resistant to atomic-oxygen attack in LEO. In fact, 3.5 wt% Si₃O₁₁ main-chain POSS polyimide eroded about 2 μm during the 3.9 year flight in LEO, whereas 32 μm of 0 wt% POSS polyimide would have eroded within 4 mos. The atomic-oxygen exposure of main-chain POSS polyimides and new side-chain POSS polyimides has shown that copolymerized POSS imparts similar AO resistance to polyimide materials regardless of POSS monomer structure.

Key words: Hyperthermal atomic oxygen, polyimide, polyhedral oligomeric silsesquioxane, POSS, space environment, polymer erosion, low Earth orbit

1. Introduction

Polyimides consist of stiff aromatic backbones and belong to a class of polymers that are called polyheterocyclics. They are known for their thermal stability, chemical solvent resistance, mechanical properties, and reasonable cost. Polyimide synthesis and processing was pioneered by workers at Dupont in the 1950's with Kapton® being the first commercially significant polyimide. Polyimides are generally formed in a polar solvent through the condensation of a dianhydride monomer and a diamine monomer. High molecular weight poly(amic acid) readily forms by the nucleophilic attack of an amino group on an anhydride carbonyl group. The poly(amic acid) then undergoes either chemical imidization or solvent evaporation followed by thermal imidization. During imidization the poly(amic acid) forms polyimide through ring-closure and concurrent loss of water.[1,2]

Many studies have been carried out on the structure-property relationships of polyimides. It has been found that subtle variations in the structures of the dianhydride and diamine components have large effects on the properties of the final polyimide. An example is the overall flexibility of the polyimide chain, as seen through parameters such as the glass transition temperature (T_g), which decreases substantially with increasing asymmetry and flexibility in the polyimide backbone.[1]

Kapton® is ubiquitous in space applications due to its temperature stability, insulation properties, IR transparency, low solar absorptance, resistance to UV damage, and excellent thermal properties.[3,4] Despite the desirable properties of Kapton®, this polyimide and all organic polymeric materials are severely degraded in low Earth orbit (LEO) as a result of reactions involving atomic oxygen (AO),[5-10] which can be more than 90% of the neutral component of the residual atmosphere at altitudes of 300-700 km.[11,12] Polymers are typically protected by the application of a coating, often silica-based, which is resistant to degradation in the presence of AO.[13-18] However, imperfections in the coating created during its deposition, or by physical damage that occurs during flight, lead to erosion of the substrate.[14,15] For this reason, alternative and self-regenerative methods of protection are sought for organic polymeric materials used in space.[19-22]

We have produced relatively durable polymers through the incorporation of polyoligomeric silsesquioxane (POSS) into Kapton® through copolymerization of POSS diamine monomers.[23-29] POSS is a unique family of nanoscale inorganic/organic hybrid cage-like structures that contain a silicon/oxygen framework ($\text{RSiO}_{1.5}$), surrounded by alkyl or aryl groups that can be utilized as polymer compatibilizers or as polymerizable functional groups.[28] We have found with POSS-F6 polyimide ("clear polyimide") and POSS-Kapton® polyimide that appropriate POSS diamines can be incorporated into the poly(amic acid) polymerization without changes to polymerization conditions, or changes to the subsequent cure cycles. Using simulated LEO environments, we have discovered that copolymerized main-chain (MC)-POSS and side-chain (SC)-POSS impart approximately the same amount of AO- resistance to Kapton® and other polyimides, regardless of POSS structure and distance from the polyimide backbone. 0 wt%, 1.75 wt%, and 3.5 wt% Si_8O_{11} MC-POSS Kapton® samples flew in LEO on the International Space Station for 3.9 years. 0 wt% POSS Kapton® completely eroded within 4 months, and a thin film of 3.5 wt% Si_8O_{11} MC-POSS Kapton® survived the flight.[25] In learning about the effect of POSS on the AO resistance and physical properties of POSS-Kaptons®, we may gain insight by considering how POSS is incorporated into the polymer and how it affects chain

packing in the polymer matrix. The inherent strength and solvent resistance of Kapton® is derived from its strong intermolecular interaction between charge transfer complexes in adjacent polymer chains. These interactions would obviously be interrupted by the incorporation of a bulky molecule such as POSS. It is believed that the POSS-diamine is randomly copolymerized into the polyimide backbone due to the expected lower reactivity of POSS-diamines relative to the Kapton® diamine monomer, oxydianiline. This is deduced from studies of the effects of monomer structure on reactivity. It has been found that dianhydrides containing bridging electron-withdrawing groups, such as a carbonyl, are more reactive than those containing bridging electron donating groups such as an oxygen (O).[1] The trend also exists, yet with less consistency, that diamine monomers containing bridging electron donating groups (O) are more reactive than those containing a bridging electron withdrawing group, such as POSS. The effect of POSS on the polymer can be somewhat elucidated by transmission electron microscopy (TEM), energy dispersive X-ray analysis (EDX), and physical property characterization. This work focuses on the physical properties of MC- and SC-POSS Kaptons®, the comparison of their AO resistance in a simulated LEO environment, and the effects of Materials International Space Station Experiment (MISSE-1 and MISSE-5) flights in LEO on MC-POSS Kapton® polyimides.

2. Experimental Details

2.1 Synthesis of Side-Chain POSS Monomers

N-{3-(R₇Si₈O₁₂)propyl}-3,5-diaminobenzamide [R = *iso*-butyl & cyclohexyl] were synthesized from 3-aminopropyl-hepta(alkyl)POSS (where alkyl is *iso*-propyl or cyclohexyl) in excess of 95% yield. The synthesis of SC-POSS has been described in detail. [30]

2.2 Synthesis of POSS-Polyimide Copolymers

Due to the ease of separation of catalyst from product, N-{3-(*iso*-butyl₇Si₈O₁₂)propyl}-3,5-diaminobenzamide was used for the copolymerization with the Kapton® monomers 4,4'-oxydianiline (ODA) and pyromellitic dianhydride (PMDA) in N,N'-dimethylacetamide (DMAc) solvent. [25, 30]

2.3 Low Earth Orbit Exposure of POSS Polyimides

MC-POSS Kaptons® containing 0, 1.75, and 3.5 wt% Si₈O₁₁, were cast and cured onto aluminium substrates and flown in LEO on the outside of the International Space Station as part of the MISSE-1. The flight experiment was launched on August 10, 2001 and was retrieved after 3.9 years. The samples were exposed to the RAM and therefore all components of the LEO environment, including AO and UV light. The step-height difference between the unexposed sample area and the neighboring exposed sample area was measured in twelve locations using profilometry. The atomic composition of sample surfaces was determined by XPS.[25] Free standing films of MC-POSS-Kaptons® containing 0, 1.75, 3.5, 5.25, and 7.0 wt % Si₈O₁₁ were sewn to a Kapton® blanket and flown in LEO on MISSE-5 for about one year. The AO fluence was estimated at 1.8×10^{20} atoms cm⁻², based on the Kapton® H recession rate during this flight.

2.4 Exposure of POSS Kapton® Polyimides to Atomic Oxygen

Ground-based AO exposures of POSS-PI samples were performed with a pulsed AO beam, operating at a repetition rate of 2 Hz and containing O atoms that were generated by the laser-induced breakdown of O₂ gas in a conical nozzle with the use of a 7-joule-per-pulse CO₂ laser. [8,26,31]. The hyperthermal beam contains neutral O atoms and molecular oxygen, with an ionic component of <0.01%. The mole fraction of AO in the beam was above 70% and, for some exposures, above 90%. Kinetic energies of the fast O atoms in the beam averaged 5.2 eV, with a full width at half maximum in the distribution of ~2 eV. Prior to exposure, samples were covered with a stainless steel mesh in order to mask areas and achieve both AO exposed and unexposed areas. The O-atom fluences of the exposures varied depending on exposure duration, but a common fluence was $\sim 2.7 \times 10^{20}$ O atoms cm⁻² for all experiments. All samples were handled in ambient air after exposure and prior to surface analysis, including etch depth determination (by profilometry) and other surface topography (AFM, SEM, and TEM) and surface chemistry measurements.

2.5 Surface Characterization of POSS- Kapton® Polyimide Films

TEM images were obtained on either a Hitachi H7600 transmission electron microscope at 120 kV or a Hitachi HD2000 STEM at Clemson University Electron Microscope Facility, SC.

2.6 Physical Property Characterization of POSS-Kapton® Polyimides

Polyimide samples were analyzed using a DMTA V from TA Instruments with a 5 °C/min temperature ramp from room temperature to 500 °C in tensile mode.[24,25] Measurements of the coefficient of thermal expansion (CTE) were taken on a thermomechanical analyzer (TMA 2940) from TA Instruments with a film fiber attachment in a nitrogen atmosphere. The cured films were cut into 15 mm by 3 mm samples, the force applied was 0.05 N & 0.10 N, and the sample was heated at 5 °C/min. The CTE was calculated as $\alpha = (\Delta L \times K)/(L \times \Delta T)$ where L = length, K = a cell constant, T = temperature in °C. Test variability was +/- 2.306 ppm °C⁻¹ based on five Kapton® H tests.

3. Results and Discussion

Two SC-POSS diamines were synthesized [30] at NAVAIR China Lake in nearly quantitative yield (>95%) from a POSS starting material that is commercially available and economical on a large scale. 3-aminopropyl-hepta(alkyl)POSS (where alkyl is *iso*-propyl or cyclohexyl) was used to produce diamines N-{3-(R₇Si₈O₁₂)propyl}-3,5-diaminobenzamide [R= *isobutyl* & cyclohexyl].[30] The SC-POSS diamine N-{3-(*iso*-butyl₇Si₈O₁₂)propyl}-3,5-diaminobenzamide was used for all polymerizations with polyimide monomers in this work. MC-POSS diamine and SC-POSS diamine were separately copolymerized with the Kapton® monomers without changes to the Kapton® polymerization procedure, or subsequent cure cycles, resulting in the POSS Kaptons® shown in Figures 1 and 2. Approximately the same weight % POSS cage was used for polymers containing both MC-POSS and SC-POSS. The amounts were inherently approximate because MC-POSS is a Si₈O₁₁ structure, while SC-POSS is a Si₈O₁₂ structure. It should be noted that 3.5 and 7 wt% POSS cage equal about 10 and 20 wt% MC-POSS diamine monomer (as reported in previous publications),[23-29] and 8.5 and 17 wt% SC-

POSS diamine monomer respectively, in the POSS polyimides.[30] This means that less SC-POSS monomer may be used, relative to MC-POSS, to deliver the equivalent amount of POSS cage into the polymer matrix.

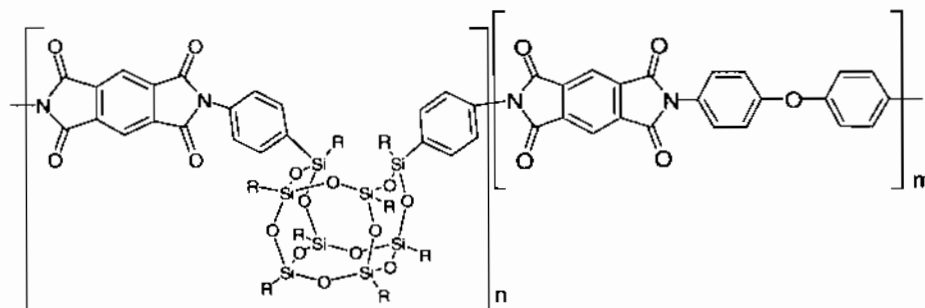


Figure 1. MC-POSS-Kapton[®] structure demonstrating the PMDA-MC-POSS repeat unit and the PMDA-ODA repeat unit. R = cyclopentyl.

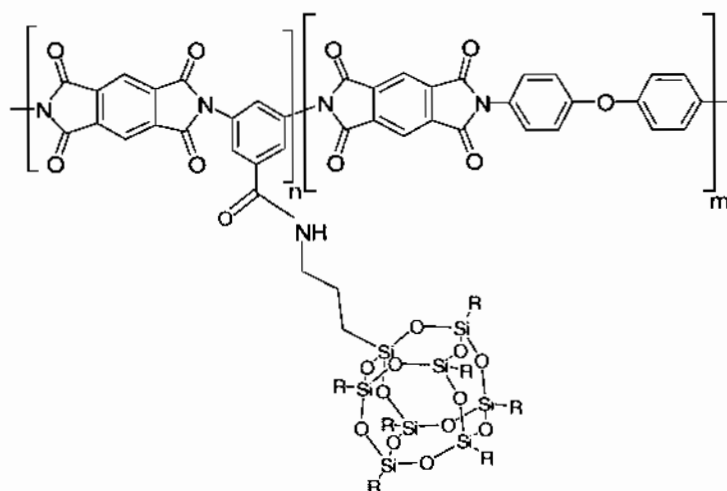


Figure 2. SC-POSS-Kapton[®] structure demonstrating the PMDA-SC-POSS repeat unit and the PMDA-ODA repeat unit. R = *iso*-butyl.

Visual comparisons of MC-POSS Kapton[®] to SC-POSS Kapton[®] show that higher weight percents of SC-POSS were copolymerized before the films showed opaque regions. Visible white aggregates formed in the 10.5 wt% Si₈O₁₁ MC-POSS Kapton[®], which was completely opaque and shattered during cure. On the other hand, 10.5 wt% Si₈O₁₂ SC-POSS Kapton[®] is transparent with areas containing visible opaque streaks. 12.3 wt% and 14 wt% Si₈O₁₂ SC-POSS Kapton[®] have increasing brittleness and areas of opaque streaks, but also have transparent flexible areas that mimic the amber color and appearance of commercial Kapton[®]. These observations imply that fine tuning of processing parameters may lead to transparent and flexible films with higher SC-POSS loadings than achieved with MC-POSS.[32] Thus far, SC-POSS has been synthesized on the 100 gram scale and a 50 μ m thick, 45 inch diameter film of 7 wt% Si₈O₁₂ SC-POSS Kapton[®] has been industrially produced by ManTech SRS Technologies in Huntsville, AL.

The addition of POSS had negligible effects on the coefficient of thermal expansion of POSS-Kapton[®] relative to 0 wt% POSS Kapton[®]. In previous work,[24, 25, 29] it was shown that commercial Kapton[®] H, 0 wt% POSS-Kapton[®], 7 wt% Si₈O₁₂ SC-POSS Kapton[®], 7 wt% Si₈O₁₂ SC-POSS Kapton[®] that was exposed to 2.3×10^{20} O atoms cm⁻², and 7 wt% Si₈O₁₁ MC-POSS Kapton[®] have CTE values of 30.25, 33.11, 35.86, 33.64, and 33.5 ppm °C⁻¹ (test variability = ± 2.306 ppm °C⁻¹). The measurements on the unexposed and AO-exposed SC-POSS Kaptons[®] were taken on different batches of material, which may have had slight variations in molecular weight and cure profile. The CTE of silica is <1 ppm °C⁻¹ which is in mismatch with the CTE of Kapton[®] and contributes to the loss of the silica layer when enduring quick temperature changes and other conditions in LEO. We have shown through a detailed examination of AO-exposed, scratched, and re-exposed 8.75 wt% MC-POSS Kapton[®] that the damaged silica layer is replenished in the presence of AO, with a maximum loss of 200 nm of the POSS Kapton[®] surface. [24, 25, 29]

The physical properties of SC-POSS-Kaptons[®] were evaluated by DMTA as shown in Figure 3. As the weight % of SC-POSS cage content increased as follows: 0, 1.75, 3.5, 7, and 8.8, the glass transition temperature decreased as follows: 407 °C, 403 °C, 406 °C, 392 °C, and 365 °C, respectively. These values are well above the use temperature of Kapton[®] in LEO, which has a maximum of 150 °C.

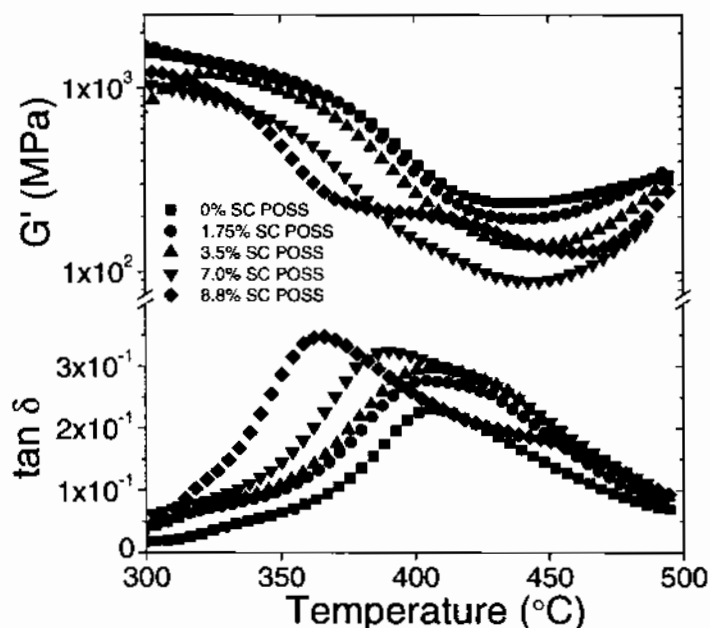


Figure 3. Dynamic mechanical thermal analysis of 0, 1.75, 3.5, 7, and 8.8 wt% Si₈O₁₂ SC-POSS Kapton[®].

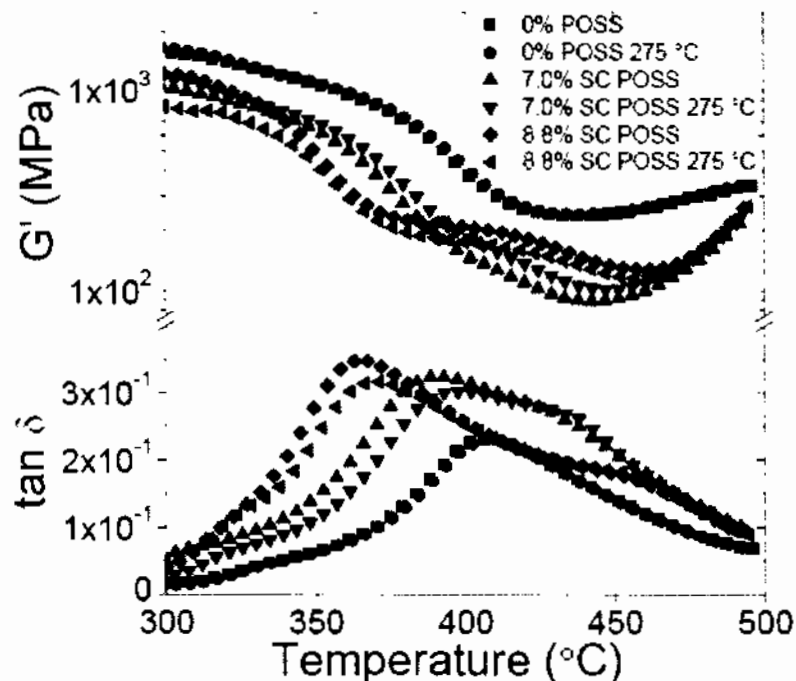


Figure 4. Dynamic mechanical thermal analysis of 0, 7, and 8.8 wt% Si_8O_{12} SC-POSS Kapton[®] with final cure at 275 °C for 2 hours (0 wt% POSS, 7.0 wt% SC-POSS, and 8.8 wt% SC-POSS), and at 275 °C for an additional 16 hours (0 wt% POSS 275 °C, 7.0 wt% SC-POSS 275 °C, and 8.8 wt% SC-POSS 275 °C).

Physical properties of MC-POSS Kaptons[®] were evaluated by DMTA and have been discussed previously.[24, 25] All T_g values, except for 8.8 wt% MC-POSS Kapton[®], were slightly lower than those for the equivalent SC-POSS Kaptons[®]. The $\tan\delta$ plots were symmetrical, and the T_g s were as follows: 420 °C for 0 wt% POSS Kapton[®], 394 °C for 3.5 wt% Si_8O_{11} MC-POSS Kapton[®], 390 °C for 7 wt% Si_8O_{11} MC-POSS Kapton[®], 383 °C for 8.75 wt% Si_8O_{11} MC-POSS Kapton[®].

To understand better the effect of POSS on imidization kinetics, a series of POSS Kaptons[®] were subjected to an extended hold at 275 °C for 16 hours. The storage modulus and $\tan\delta$ curves versus temperature are shown in Figure 4. The T_g increased for 7.0 and 8.8% SC-POSS-Kapton[®] after the extended cure period. While the storage modulus and $\tan\delta$ curves for the Kapton[®] without POSS are unchanged, *iso*-Butyl POSS has been shown to decrease the T_g and increase entanglement density in tethered copolymers because of the increased free volume created by the POSS. [28] Yet, Figure 4 represents the effect that POSS has on the imidization kinetics of the polyimide. As the amount of SC-POSS increases, the ability for a strong charge complex between carbonyls and nitrogen groups in the polyimide backbones are diminished. At an extended cure hold, further imidization occurs. This is demonstrated by the increase in T_g , as the bulk polymer mobility is decreased.

Further insight into POSS dispersion and POSS-POSS aggregation may be seen by TEM imaging of POSS Kapton[®] films. Wei et al. carried out TEM imaging on POSS end-capped Kapton[®] films, which were directionally blade-cast before cure. It was reported that POSS-POSS aggregates formed lamellae about 2-3 nm wide, as seen by layers of dark lines

perpendicular to the film plane and casting direction, as well as by dark dots when the image was taken parallel to the film plane and casting direction. Interestingly, the Si-Si distance in a POSS cage is 0.5 nm and the width of a POSS cage with cyclohexyl groups is 1.5 nm.

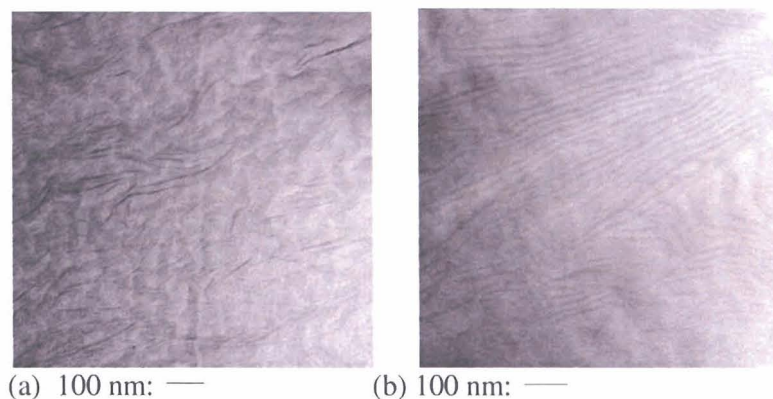


Figure 5. TEM image of 8.8 wt % Si_8O_{11} MC-POSS Kapton[®] measured at (a) HV = 120 kV, Direct Magnification: 150,000x, and (b) HV = 120 kV, Direct Magnification: 200,000x.

In our study, the films were solvent-cast by pouring the POSS poly(amic acid) onto a glass plate with no blade casting or forced directionality. As seen in Figures 5 and 6, the 7.0 and 8.8 wt% Si_8O_{11} MC-POSS Kapton[®] films appear to have areas of good POSS dispersion and areas with darkened POSS-POSS aggregates, creating lamellae that are approximately 5 nm wide. There are also a very small number of darkened spheres approximately 5 nm wide. Fabrication of MC-POSS-Kaptons[®] has been carried out with much iteration over a multi-year time span, resulting in films with consistent physical properties and surface morphologies per MC-POSS content. Further investigation of these materials by energy dispersive x-ray analysis (EDX) may clarify the composition of the darkened areas.

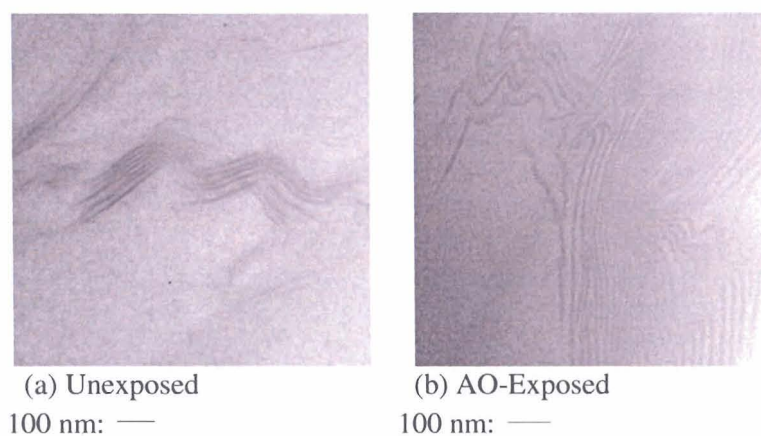


Figure 6. TEM image of 7.0 wt% Si_8O_{11} MC-POSS Kapton[®] measured at (a) HV = 120 kV, Direct Magnification: 150,000x, and (b) HV = 120 kV, Direct Magnification: 200,000x.

The SC-POSS Kaptons[®] result in differing TEM images per weight % POSS. These newer materials are under analysis for characteristic morphologies. Despite the differences between MC- and SC-POSS Kaptons[®], the physical properties are fairly similar. As shown below, the AO resistance data are better correlated with weight % POSS than the position of the POSS co-monomer, relative to the polymer chain.

The series of SC-POSS Kaptons[®] was exposed to AO with a total fluence of 2.7×10^{20} O atoms cm^{-2} . Results, in Table 1, indicate dramatic decreases in surface erosion with increasing POSS content. In an AO exposure with a total fluence of 3.53×10^{20} O atoms cm^{-2} , 7 wt% Si_8O_{12} SC-POSS Kapton[®] had an erosion yield that was 3.3 wt% of Kapton[®] H. In a separate AO exposure with a total fluence of 4.10×10^{20} O atoms cm^{-2} , 7 wt% Si_8O_{11} MC-POSS Kapton[®] had an erosion yield that was 3.8 % of Kapton[®] H. The MC- and SC-POSS Kaptons[®] were also exposed side by side to 2.68×10^{20} O atoms cm^{-2} . The % erosion of the POSS Kaptons[®] relative to Kapton[®] H were $4.25 \pm 0.48\%$ for 7 wt% Si_8O_{11} MC-POSS Kapton[®] and $4.86 \pm 0.47\%$ for 7 wt% Si_8O_{12} SC-POSS Kapton[®]. The laboratory-scale synthesis of the polymer films is likely to produce slight differences in molecular weights and cure cycles, thus potentially having minor affects on the AO erosion of the materials. The existing data indicate that the AO-induced erosion yields of MC-POSS Kapton[®] and SC-POSS Kapton[®] are comparable. Thus, the level of erosion resistance afforded by POSS appears to depend on the wt% of the monomer and not how it is bound to the polymer chain.

Table 1. Laboratory AO Erosion Data of SC-POSS Kapton[®] Polyimides

Weight % Si_8O_{12} in SC-POSS Kapton [®]	Kapton [®] - Equivalent Fluence / 10^{20} O atoms cm^{-2}	Erosion Depth (μm)	% Erosion of Kapton [®] H Witness Sample
1.75	2.71	1.99 ± 0.01	24.5
3.5	2.66	1.29 ± 0.05	16.15
7.0	2.68	0.390 ± 0.04	4.9
8.8	2.68	0.132 ± 0.02	1.64
10.5	2.71	0.249 ± 0.03	3.06
12.3	2.71	0.113 ± 0.03	1.39
14.0	2.71	Undetectable	~ 0

Table 2. MISSE-1 Flight MC-POSS Kapton[®] Erosion Data

Sample	^a Average Step Height in microns	Standard Deviation in microns	Erosion in 3.9 years
0 wt % Si_8O_{11} MC-POSS Kapton [®]	32.6	0.9	^b 240
1.75 wt % Si_8O_{11} MC-POSS Kapton [®]	5.8	1.3	5.8
3.5 wt % Si_8O_{11} MC-POSS Kapton [®]	2.1	0.3	2.1

^aData from 12 step-height measurements around the perimeter of exposed area of circular sample with neighboring outer ring masked and not exposed to LEO.

^b0 % POSS-PI total erosion estimated using AO fluence. Estimate for total flight is 8×10^{21} atoms/ cm^2 .

MC-POSS Kapton[®] films were flown on the Materials International Space Station Experiment – 1 (MISSE-1) for 3.9 years. The samples were placed such that they experienced the ram direction. Various images of the samples were taken throughout the flight, and these show that the 0 wt% POSS Kapton[®] was completely eroded in less than four months. The step heights from the unexposed area and the neighboring exposed portion of the sample were measured in 12 places around the circumference of each exposed sample. From these measurements, it was determined that the thickness of the masked 0 wt% POSS Kapton[®] was $32.6 \pm 0.9 \mu\text{m}$. The erosion data are shown in Table 2, and SEM images of the flown 1.75 wt%, and 3.5 wt% Si₈O₁₁ MC-POSS Kaptons[®] are shown in Figures 7 and 8. It was determined by XPS that the atomic percentages of the top 10 nm of both POSS Kapton[®] films were 34% Si, 59% O, and 7% C for both the 1.75 and 3.5 wt% Si₈O₁₁ MC-POSS Kapton[®] samples.

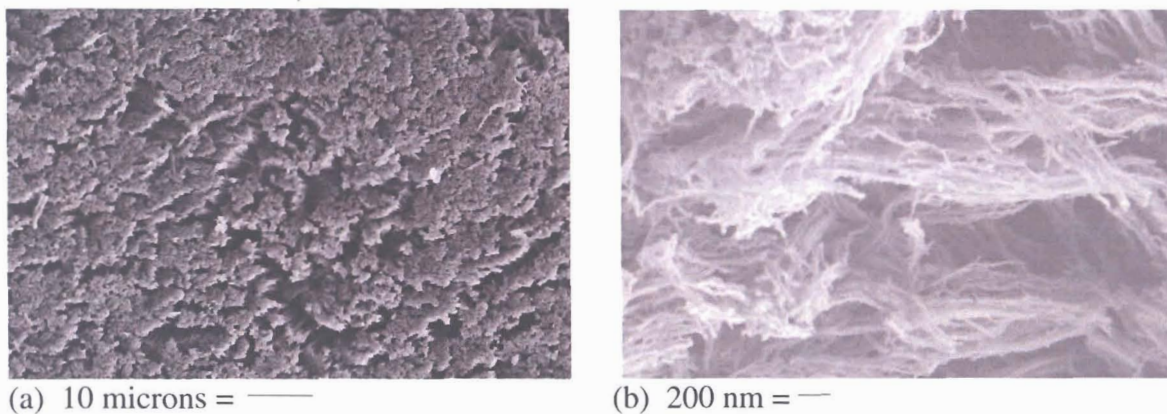


Figure 7. Scanning electron micrographs of 1.75 wt% Si₈O₁₁ MC-POSS Kapton[®] flown on MISSE-1.

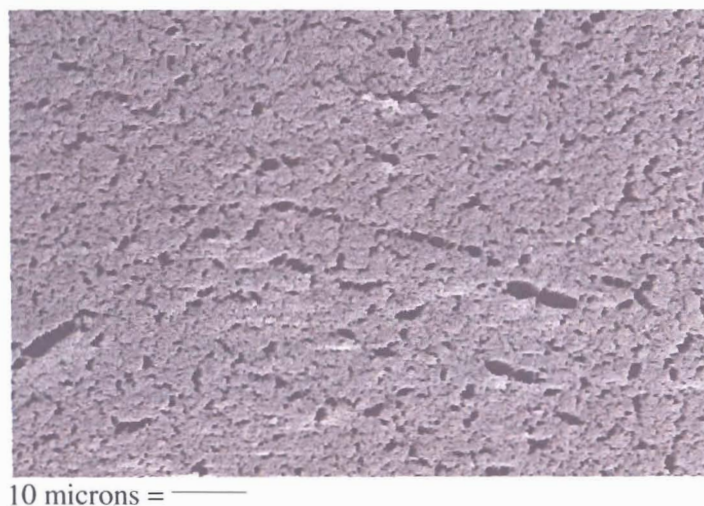


Figure 8. Scanning electron micrograph of 3.5 wt% Si₈O₁₁ MC-POSS Kapton[®] flown on MISSE-1.

0, 1.75, 3.5, 5.25, and 7.0 wt% Si₈O₁₁ MC-POSS Kaptons[®] were flown on MISSE-5 in LEO for about one year and experienced an approximate AO fluence of 1.8×10^{20} atoms cm⁻². Samples were located on the top side of the International Space Station and, although they were

exposed to all components of the LEO environment, they were situated such that a part of the ISS obstructed the ram and therefore reduced the AO fluence. All samples survived, and erosion depths decreased with increasing POSS content, as shown in Table 3. As is commonly observed for AO exposures in simulated LEO experiments, the commercial Kapton[®] H eroded less than the 0 wt% POSS Kapton[®], which was synthesized by the same technique as the POSS Kaptons[®].

Table 3. MISSE-5 Flight Sample Erosion Data

Sample	Erosion Depth (μm)
Kapton H	2.42 ± 0.47
0 wt % POSS Kapton	2.89 ± 0.59
1.75 wt % Si ₈ O ₁₁ MC-POSS Kapton	1.15 ± 0.21
3.5 wt % Si ₈ O ₁₁ MC-POSS Kapton	0.44 ± 0.19
5.3 wt % Si ₈ O ₁₁ MC-POSS Kapton	0.31 ± 0.18
7.0 wt % Si ₈ O ₁₁ MC-POSS Kapton	0.25 ± 0.11

4. Conclusion

MC- and SC-POSS-Kaptons[®] were found to have similar physical properties and comparable erosion yields in laboratory AO exposures. It was found that the incorporation of POSS slightly reduces the glass transition temperature (T_g) of Kapton[®]; however, T_g values of POSS Kaptons[®] are well above the temperatures experienced by materials in many applications. The modulus, T_g, and CTE of SC-POSS Kaptons[®] were determined before and after exposure to atomic oxygen and are comparable to the values of these properties for Kapton[®] H. The SC-POSS monomer was synthesized by facile methods, transparent flexible films can be prepared at higher SC-POSS loadings than MC-POSS, and a SC-POSS Kapton[®] sheet has been industrially fabricated. MC-POSS-Kapton[®] samples were flown in low Earth orbit for nearly four years on MISSE-1 and for about one year on MISSE-5. The 0 wt% POSS Kapton[®] sample completely eroded within four months, while a thin film of the 3.5 wt% Si₈O₁₁ POSS Kapton[®] remained after flight, thereby demonstrating significantly enhanced space durability for the POSS Kapton[®] over pure Kapton[®]. MC-POSS Kaptons[®] were also flown on MISSE-5 and again exhibited decreasing erosion in low Earth orbit with increasing POSS content.

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